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LITHIUM BATTERY SYSTEMS: EXAMINATION OF THE IODINE PENTOXIDE CA--ETC(U)

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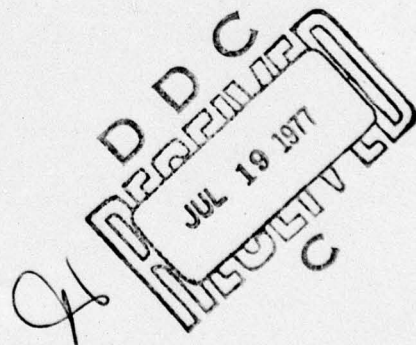
# DEFENCE RESEARCH ESTABLISHMENT OTTAWA

DREO REPORT NO. 760  
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## LITHIUM BATTERY SYSTEMS: EXAMINATION OF THE IODINE PENTOXIDE CATHODE

by

J.R. Coleman and G.D. Nagy



PROJECT NO.  
54-80-08

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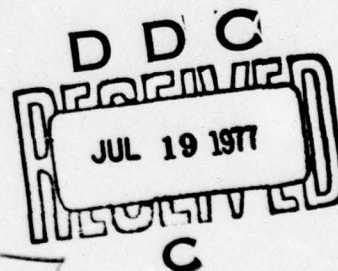
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LITHIUM BATTERY SYSTEMS: EXAMINATION OF  
THE IODINE PENTOXIDE CATHODE

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54-80-08

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ABSTRACT

The electrochemical system lithium-iodine pentoxide, attractive because of its high theoretical energy density, was investigated, employing as electrolyte a variety of salts dissolved in polar organic solvents. Iodine pentoxide blended with graphite and pressed on an expanded silver grid served as cathode; the anodes were made by pressing lithium ribbon onto an expanded nickel grid.

Of the salt-solvent combinations tried, potassium perchlorate dissolved in dimethylsulfoxide was most satisfactory; even with this combination the fraction of the theoretical energy density realized amounted at most to about 12%. Chemical investigations showed that iodine pentoxide in dimethylsulfoxide may enter into several kinds of reactions, all of which lead to its conversion to the electrochemically inactive iodate ion. One sixth or 17% of the pentoxide appeared to be the most that can in fact be discharged. This fact, coupled with its poor activated stand properties and moderate drain capability make it improbable that the system could be developed into a practical battery.

RÉSUMÉ

On a examiné le système électrochimique au lithium et au pentoxyde d'iode qui est intéressant à cause de sa grande densité d'énergie théorique. On a utilisé comme électrolyte une variété de sels dissous dans des solvants organiques polaires. La cathode est formée de pentoxyde d'iode mélangé à du graphite, pressé sur une grille allongée en argent, l'anode est composée en pressant une feuille de lithium sur une grille allongée en nickel.

De toutes les combinaisons de sel et de solvant étudiées, la plus satisfaisante était le perchlorate de potassium dissous dans le diméthylsulfoxyde; même là, le pourcentage maximal de densité d'énergie théorique n'était que de 12 p.c. Les expériences ont montré que la solution  $I_2O_5/DMSO$  peut entrer dans diverses sortes de réactions chimiques qui mènent toutes à sa conversion en ion iodé neutre. Il semble impossible d'obtenir une

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décharge de plus de 1/6 ou 17 p.c. du pentoxyde. Sa conservation inférieure de charge après activation et sa capacité de décharge moyenne rendent improbable l'utilisation pratique de ce système de batterie.



### INTRODUCTION

The work described below was carried out during a period of widespread interest in non-aqueous battery systems, and was suspended when efforts in this field suffered a decline a few years ago. More recently there has been a renewal of interest in the subject, stimulated by development of the lithium-sulfur dioxide (1) and lithium-thionyl chloride (2,3) batteries, which operate at high efficiency, so that the predicted high energy densities advanced as justification for these investigations were for the first time being approached. In the wake of these major developments fresh interest was shown in specialized non-aqueous systems for moderate drain applications. Among these are batteries based on cupric sulfide (4) molybdc oxide (5-7), carbon and graphite fluorides (8,9) and vanadium pentoxide (10). The chemical reactions occurring in these latter systems are complex and for the most part not understood; and with the proposed resumption of lithium battery work at DREO it seemed desirable to record our experiments directed to understanding the cathodic reactions at the iodine pentoxide electrode.

The starting point of this investigation of iodine pentoxide was a report by Knapp (11), who described a number of cathode-anode-organic solvent-electrolyte combinations, and concluded that several acid anhydrides showed promise as cathodic depolarizers. Briefly, the cathodes he employed fell into one of several classes: acid anhydrides, salts and reducible metal oxides ( $\text{HgSO}_4$ ,  $\text{Ag}_2\text{O}$ ), organic depolarizers, and sulfur. These materials were blended with graphite or other conductive carbon and compressed on a silver or nickel grid. The most suitable anode was lithium ribbon, also compressed on a metal grid. The electrolyte system consisted of one of the following organic solvents: dimethylsulfoxide (DMSO), propylene carbonate (PC) or acetonitrile, containing potassium perchlorate ( $\text{KClO}_4$ ), lithium bromide ( $\text{LiBr}$ ), magnesium perchlorate ( $\text{Mg}(\text{ClO}_4)_2$ ) or potassium thiocyanate ( $\text{KSCN}$ ) as the solute. The most satisfactory combinations were described in a patent application (12) and include the following components:

TABLE I

Non-Aqueous Cell Combinations Described by Knapp

Cathode:	$\text{CrO}_3$ , $\text{I}_2\text{O}_5$ , $\text{V}_2\text{O}_5$ , $\text{MoO}_3$ , m-dinitrobenzene
Solvent:	DMSO, PC, DMSO-PC mixtures
Electrolyte:	$\text{KClO}_4$ , $\text{LiBr}$ , $\text{Mg}(\text{ClO}_4)_2$ , $\text{KSCN}$
Anode:	Li Metal

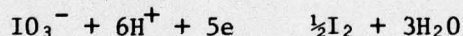
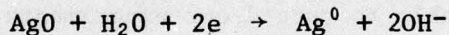


Based on open-circuit voltage measurements in DMSO-KClO<sub>4</sub> (eg. 3.85V for the Li/I<sub>2</sub>O<sub>5</sub> combination) and stoichiometric amounts of materials, energy densities are quite large. For the four acid anhydrides above, coupled with a lithium anode, these figures are 1558, 1251, 1490 and 733 watt-hours per pound, respectively.

Several problems were pointed out by Knapp:

(i) The coulombic efficiency of utilization actually observed for these depolarizers to an arbitrary cell cut-off voltage of 1.5 volts fell far short of the theoretical. Thus for I<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub> the coulombic efficiency was apparently\* 1.7% and 2.8% at the moderate current density of 2.5 mA/cm<sup>2</sup>; the energy efficiency, because the average operating voltage is only about 2/3 the open circuit voltage, was lower still. Thus only a very small fraction of the depolarizer was used before the voltage fell to an unacceptable value.

(ii) The energy densities calculated above assumed reduction to the valence states of I<sup>0</sup> for I<sub>2</sub>O<sub>5</sub>, Cr<sup>++</sup> for CrO<sub>3</sub>, V<sup>++</sup> for V<sub>2</sub>O<sub>5</sub> and Mo<sup>+++</sup> for MoO<sub>3</sub>; in fact, however, no investigations of the actual reduction products were made. Also, in an aqueous or protonic solvent, such reactions as the following could formally occur on reduction of an oxygen-containing cathodic constituent:



but in aprotic solvents such mechanisms were not possible, and nothing was known of the fate of the oxygen in such species as I<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>, or indeed of any aspect whatever of the reduction mechanisms.

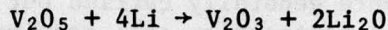
More recently, advances have been made with several of these cathode systems. V<sub>2</sub>O<sub>5</sub> has been employed in a reserve type of battery under development by Honeywell (10), and this material and MoO<sub>3</sub> have been re-investigated by several workers. Dampier (6), and Campanella and Pistoia (5) have obtained quite reasonable coulombic efficiencies, employing MoO<sub>3</sub>; the latter workers have thrown some light on the mechanism of MoO<sub>3</sub> reduction, which is more complex than a simple reduction to Mo<sub>2</sub>O<sub>5</sub> (i.e. Mo<sup>+5</sup>) or MoO<sub>2</sub> (Mo<sup>+4</sup>). Campanella and Pistoia pointed out that the working potential of the system Li/PC-AlCl<sub>4</sub>/MoO<sub>3</sub> is higher than the calculated open circuit potentials assuming such products as Li<sub>2</sub>O, MoO<sub>2</sub> and Mo<sub>2</sub>O<sub>5</sub>, and suggest that complexing with the electrolyte occurs. Dey (13) working with PC-LiClO<sub>4</sub> as the solvent-electrolyte system, reported efficiencies for the Li/MoO<sub>3</sub> and Li/V<sub>2</sub>O<sub>5</sub>

\*In reference (11) the weight of cathode material used is not stated; these figures are calculated by combining information from references (11) and (12), and though probably correct are a little suspect. In any case, as confirmed in the present work, only a few percent of the material is utilized to a practical end-voltage.

couples of 70-80% and 60-70% respectively, assuming the following reactions:



and



but presented no evidence that these were in fact the reactions that occurred.

As the chemistry of  $\text{I}_2\text{O}_5$  is more familiar than that of the other acid anhydrides, and the number of stable oxidation states is small, it was decided to investigate some of the problems mentioned above, using this depolarizer.

#### EXPERIMENTAL

The procedures followed closely those of Knapp in most details. The cathodic mixes contained  $\text{I}_2\text{O}_5$  and up to 40% by weight of a commercial graphite\*, blended in a paint shaker with glass beads. Care had to be taken to avoid too prolonged shaking, as frictional heat initiates an exothermic decomposition of  $\text{I}_2\text{O}_5$ . An amount of 1.2 to 2.0 g of the blended dry mix was spread on both sides of an expanded nickel or silver grid, 3.17 cm x 3.17 cm (10.0 cm<sup>2</sup>), with an attached tab, and wrapped in an envelope of No. 2 Whatman filter paper. Plates assembled in this manner were then pressed at 1300 to 7700 psi and stored in a desiccator until discharge.

Lithium ribbon was pressed at 2600 psi on expanded nickel grids cut the same size as the cathode grids, degreased in benzene. The lithium anodes were scraped with a scalpel just before insertion in the cell. The weight of lithium taken, about 0.36 g, is considerably greater than the stoichiometrically required amount, to ensure that the cell is cathode limited.

Electrolyte solutions were usually prepared by mixing anhydrous salts and solvents in the ratio of 1 mole to 1000 ml. These are referred to here as one molar, although this is only approximately true. In a few experiments using  $\text{KClO}_4$  in DMSO, electrolyte concentrations were varied over a

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\*Micro 850, a product of Asbury Graphite Mills, Asbury, N.J.



tenfold range (see for example, Table X); and a number of saturated solutions of less than one molar were used (Table II).

A variety of experiments were conducted to determine the fate of the oxygen in the  $I_2O_5$ . These will be described in the appropriate section.

Discharges were generally carried out with one cathode sandwiched between two anodes in a rectangular cell requiring about 25 ml electrolyte to cover the plates. Constant current was maintained by a manually adjusted external resistor, and the cell voltage was measured with a General Radio 1230A electrometer. Control experiments showed that neither exhaustive drying of the system nor addition of small amounts of water made much difference in the results, and runs were carried out in open cells.

A number of variations were made in this basic procedure for specific purposes: larger cells were used to study the effect of electrolyte volume on efficiency; zinc was used in place of lithium in several experiments; and additions of several materials were made to the cathode in an attempt to increase utilization.

A three-electrode cell with an auxiliary cathode or anode to serve as reference was used in certain polarization studies. Details of the experimental procedures are given in the Polarization Experiments section.

## RESULTS AND DISCUSSION

### VARIATION IN DEPOLARIZER AND ELECTROLYTE

It was decided first to check on various electrolyte combinations to find the most suitable before attempting to make changes in the cathode itself. For this purpose cathodes were made containing 2 g of a 10:1  $I_2O_5$ : graphite mix and were pressed at 7700 psi, a pressure that ensured good mechanical stability.

Table II summarizes discharges for  $I_2O_5$  cathodes in various solvent-solute combinations. For comparison, a number of cathodes similarly made, but containing  $I_2$  in place of  $I_2O_5$ , were made and discharged (runs J, K, L).

Curves 1 and 2 of Figure 1 show typical discharge curves for  $I_2O_5$  and  $I_2$  (runs A and J of Table II). For curve 1, the coulombic efficiency to 2.0 volts is calculated as 2.8%, assuming a 5-electron change per iodine atom ( $I^{+5} \rightarrow I^0$ ) or a 10-electron change per molecule, so that the equivalent weight of  $I_2O_5$  is 33.38. The problem of low utilization referred to by Knapp is apparent. The general behaviour closely resembled that reported by Knapp.



TABLE II  
Variations in Depolarizer and Electrolyte

Run	Cathode	Solvent Electrolyte	Min. to 2.0 Volts	Percent Utilization	Remarks
A	I <sub>2</sub> O <sub>5</sub>	DMSO-KClO <sub>4</sub>	97	2.8	In run B, I <sub>2</sub> O <sub>5</sub> pulverized in dry box before blending with graphite; in all other runs, I <sub>2</sub> O <sub>5</sub> used as received.
B	"	"	151	4.3	
C	"	DMSO-LiBr	22	0.6	
D	"	PC-KSCN	6	0.17	
E	"	PC sat'd KClO <sub>4</sub>	∞	∞	
F	"	PC-LiBr	∞	∞	
G	"	DMSO-KSCN	50	1.4	
H	"	DMF*0.8M KClO <sub>4</sub>	32	0.91	
I	"	DMF-LiBr	∞	∞	
J	I <sub>2</sub>	DMSO-KClO <sub>4</sub>	162	17.6	260 minutes to 1.95V = 28.2% efficiency.
K	I <sub>2</sub>	PC sat'd KClO <sub>4</sub>	150	16.3	
L	I <sub>2</sub>	DMSO-LiBr	84	9.1	
M	I <sub>2</sub> O <sub>5</sub>	DMSO-0.5M KNO <sub>3</sub>	66	2.7	
N	"	DMSO-LiCl	<1	0	
O	"	DMSO-0.25M LiCl	<1	0	
P	"	DMSO-KI	14	0.6	
Q	"	DMSO-0.5M KI	8	0.4	

NOTE: All discharges at 25mA. Two lithium anodes, one cathode. Runs A-L, 2.0g, 10:1 I<sub>2</sub>O<sub>5</sub>:C or I<sub>2</sub>:C, 7700 psi (Runs M-Q, 1.6g, 3:1 I<sub>2</sub>O<sub>5</sub>:C, 1300 psi). Solutions 1M in electrolyte except as noted.

\* DMF = N,N dimethylformamide.

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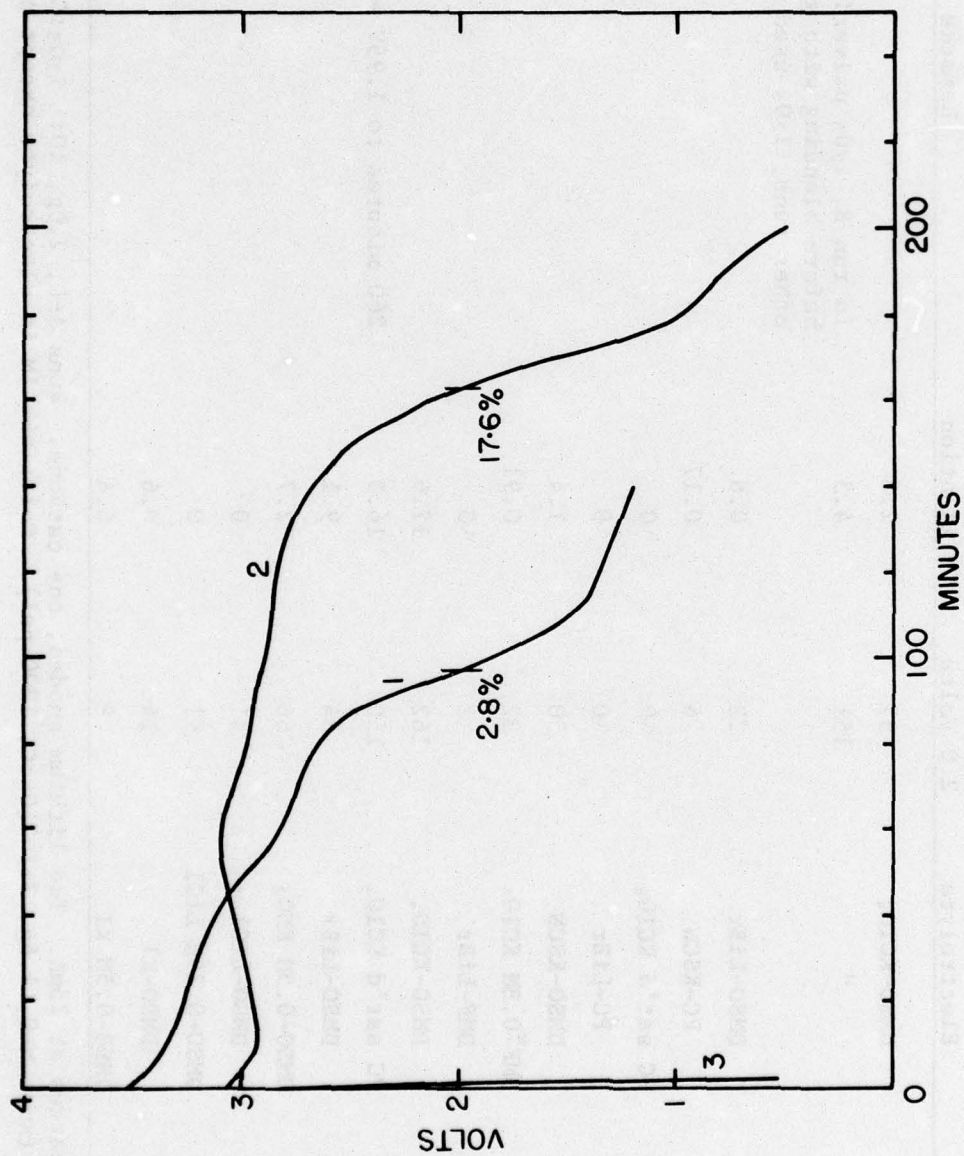


Fig. 1: Typical discharges of  $I_2O_5$  (1),  $I_2$  (2) and  $KIO_3$  (3) cathode systems in DMSO-1M  $KClO_4$ . Two lithium anodes, current 25 mA. Other conditions are described in text. The percentages represent efficiency of coulombic utilization to a 2 volt cutoff.

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The run time to 2.0 volts of the iodine cathode (curve 2) is significantly longer than that of curve 1, and considering the much higher equivalent weight of iodine (126.9), the superiority in utilization is greater still (17.6% compared to 2.8%).

From an examination of runs (A)-(G) it is seen that PC as a solvent functions very poorly compared to DMSO with  $\text{KClO}_4$ , LiBr or KSCN as electrolyte. Runs (H) and (I) compared with runs (A)-(G) show that DMF is in general better than PC, but not as good as DMSO. With all solvents,  $\text{KClO}_4$  is apparently the preferred electrolyte. Run (B) demonstrates incidentally the improvement achievable by increasing the state of subdivision of the  $\text{I}_2\text{O}_5$ .

From runs (J)-(L) it is seen that  $\text{I}_2$  outperforms  $\text{I}_2\text{O}_5$  in the solvent-solute combinations tried; furthermore its performance is not nearly so sensitive to the nature of solvent or electrolyte.

The direct use of iodine as a depolarizer (14) presents difficulties by reason of its volatility and solubility in organic solvents. The reaction of iodate and iodide to liberate iodine is well known, and it was thought that iodine might be generated from  $\text{I}_2\text{O}_5$  and iodide if a soluble iodide such as KI were introduced either in the electrolyte or the cathode. A number of variations of this idea were attempted, but in all cases performance was worse than when the KI was omitted.

It was observed early in the work that  $\text{I}_2\text{O}_5$  dissolved slowly in DMSO on stirring to at least 10% by weight, forming a sticky viscous fluid, and also that after a few hours a reaction began between solvent and solute with the liberation of  $\text{I}_2$ . In propylene carbonate, however, the solubility is only about  $8 \times 10^{-2}$  g/litre, and no liberation of iodine was observed.

These facts suggested at first that the relatively good (though for practical purposes unsatisfactory) performance of  $\text{I}_2\text{O}_5$  with DMSO as solvent compared to PC was due in part to the fact that it was soluble in the former and could react to produce  $\text{I}_2$ , which is itself the electrochemically active species. However, the discharge reaction is primarily electrochemical reduction of  $\text{I}_2\text{O}_5$ . If an  $\text{I}_2\text{O}_5$  cathode is placed in DMSO- $\text{KClO}_4$  electrolyte and left on open circuit, no visible change is noted for some time; when discharge begins, an immediate orange-brown stain ( $\text{I}_2$ ) is seen in the filter-paper envelope.

Curve 3 of Figure 1 ( $\text{KIO}_3/\text{DMSO-KClO}_4/\text{Li}$ ) shows that  $\text{KIO}_3$  is electrochemically quite inactive in this organic solvent. This was thought to be due to the insolubility of  $\text{KIO}_3$ . Cathodes were prepared with more soluble iodates,  $\text{NH}_4\text{IO}_3$  and  $(\text{CH}_3)_4\text{NIO}_3$ . However, these proved useless in DMSO- $\text{KClO}_4$  electrolyte.

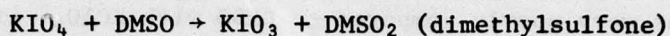
Potassium periodate ( $\text{KIO}_4$ ) seemed attractive as a possible depolarizer because of the higher oxidation state of iodine (+7).

The cell

$\text{KIO}_4\text{-C/DMSO, LiBr or KClO}_4/\text{Li}$



gave a very short discharge. Moreover, while  $\text{KIO}_4$  dissolved initially in DMSO, a white precipitate identified as  $\text{KIO}_3$  shortly came out, and it appeared probable that the reaction



had occurred. The ease of oxidation of DMSO by various inorganic oxidants has been noted (15).

#### VARIATIONS IN CATHODE PREPARATION AND DISCHARGE CONDITIONS

The best performance reported in Table II was shown in runs A and B, using a cathode made of 2.0g of 10:1  $\text{I}_2\text{O}_5$ :graphite compressed at 7700 psi on a silver grid, and discharged in DMSO- $\text{KClO}_4$ .

This section records the results of a systematic study of all variables in the preparation and discharge of cathodes, in part to extend knowledge over a wider range of operating conditions, and in part to improve the still exceedingly low efficiency of utilization. In the tables that follow, the column "No." indicates the number of duplicate runs carried out with each set of conditions. Except in Table X the electrolyte is 1 molar  $\text{KClO}_4$  in DMSO.

#### COMPACTING PRESSURE

Table III shows the improvement in performance that results as the compacting pressure is reduced from 7700 psi. This improvement is presumably due to increased ease of cathode penetration by the solvent. A practical lower limit is imposed, of course, by the minimum pressure required to make the cathode material adhere firmly to the grid.

#### $\text{I}_2\text{O}_5$ -GRAPHITE RATIO

In previous work, a 10:1  $\text{I}_2\text{O}_5$ :graphite ratio had been regularly employed. Using now the lower compacting pressure (1300 psi), this ratio was varied downward, and a marked increase in utilization observed (Table III and IV). In the second study (Table V) the weight of mix was varied so as to

TABLE III

Effect of Compression on Cathode Performance

Mix Composition I <sub>2</sub> O <sub>5</sub> :C	Compression psi	Amount of mix, g.	No.	% Coulombic Efficiency
10:1	7700	2	8	1.4
10:1	2600	2	3	1.7
10:1	1300	2	5	2.0
5:1	7700	2	6	3.0
5:1	1300	2	4	4.2

TABLE IV

Effect of Varying Cathode Compositions. Weight of Mix Constant at 2g.

Mix Composition	Compression psi	Wt of Active Material, g.	No.	% Coulombic Efficiency
10:1	1300	1.81	5	2.0
5:1	"	1.67	4	4.2
3:1	"	1.5	3	7.0
1.5:1	"	1.2	4	8.1

TABLE V

Effect of Varying Cathode Composition. Weight of Active Material 1.6g.

Mix Composition	Compression psi	No.	% Coulombic Efficiency
5:1	1300	4	3.4
3:1	"	6	6.4
1.5:1	"	4	8.1



maintain a constant weight of active material, and a similar improvement noted. There is evidently an advantage in increasing the amount of conductive carbon at least up to the point at which the weight and volume of electrochemically inactive material becomes a handicap. The most generally suitable conditions of preparation, and those used in the rest of the work unless otherwise stated, are a 3:1  $I_2O_5$ :graphite ratio and a compression of 1300 psi.

### LOADING

The effect of varying the cathode loading (i.e. the amount of mix) is contrary to what would be expected, for the first two mix ratios of Table VI, in that thinner cathodes gave lower utilization. The reason for this is not known with certainty. It is possible that with lightly loaded cathodes, one is compressing only the grid and not the powder in the grid interstices. The third mix ratio (1.5:1) has a larger amount of the bulky, low density graphite, so that compaction might be effective down to lower loading weights; and the fact that in this case performance improves with lower loading lends some support to the suggestion made above.

TABLE VI

Effect of Cathode Loading

Mix Composition	Compression psi	Mix wt g	No.	% Coulombic Efficiency
5:1	1300	2	4	4.2
5:1	"	1.44	4	3.4
3:1	"	2	3	7.0
3:1	"	1.6	6	6.4
1.5:1	"	2	4	8.1
1.5:1	"	1.2	4	10.0

### GRID

Grids of expanded copper, nickel and several sizes of silver were used. Adhesion to copper and nickel appeared not to be as satisfactory as to silver. In addition, when copper grids were used the open circuit voltage fell from 3.7 to 3.0 volts after 20 minutes. It is recognized that adhesion



of cathode material may be related to the stiffness or springiness of the grid, as well as to its chemical nature, but in any case silver is evidently the best material.

#### ACTIVATED STAND

Cathodes were made, employing silver grids and 1.6 grams of 3:1  $I_2O_5$ :graphite compressed at 1300 psi. These were immersed in the electrolyte for varying periods of time before beginning discharge, with the results noted in Table VII. Wet stand is detrimental to cell performance, suggesting the occurrence of a non-electrochemical reaction between cathode material and electrolyte. It has already been noted that  $I_2O_5$  dissolves slowly in DMSO with the formation of iodine; but the effect is more complex than this would imply, since at first sight iodine might be expected to enhance the reaction. Possibly the formation of a very viscous solution in and near the electrode reduces ionic mobility and so diminishes performance.

TABLE VII

Effect of Activated Stand

Mix Composition: 3:1  $I_2O_5$ :C      Dry Mix: 1.6g      1300 psi

Hours Stand	No.	% Coulombic Efficiency
0	7	5.6
1	3	5.2
2	3	5.2
4	3	4.2

#### TEMPERATURE

DMSO freezes at 18°C; hence, discharges conducted at room temperature, as heretofore, are near the lower extreme of the liquid range. One might expect some improvement in runout at higher temperature because of the resulting increase in electrolyte conductivity. However, as Table VIII indicates, performance is, if anything, somewhat worse. Various explanations for this can be devised, but again nothing certain is known.

TABLE VIII

## Effect of Temperature

Mix Composition	Compression psi	No.	O.C.V.	% Coulombic Efficiency	Comparison With Room Temperature Performance
(a) 33°C					
10:1	7700	2	3.90	1.5	Higher O.C.V. No difference in % utilization.
(b) 52.5°C					
5:1	1300	2	3.80	2.2	Higher O.C.V. % utilization about 50% lower.
3:1	1300	1	3.85	3.6	Higher O.C.V. % utilization about 45% lower.

CURRENT DENSITY

Employing again cathodes made as in Table VII, discharges were conducted over a sixfold range of current density, with the results shown in Table IX. It is apparent that at greater than a modest current drain cathode performance suffers.

TABLE IX

## Effect of Varying Current Density

Mix Composition: 3:1 I <sub>2</sub> O <sub>5</sub> :C      Dry Mix 1.6g      1300 psi			
I mA	C.D. mA/cm <sup>2</sup>	No.	% Coulombic Efficiency
12.5	1.38	1	12.1
25	2.76	6	6.4
75	8.23	2	3.8



### ELECTROLYTE CONCENTRATION

In the experiments reported in Table X, the electrolyte ( $\text{KClO}_4$ ) concentration was varied from 1M to 0.1M. It can be seen that 1M  $\text{KClO}_4$  is the best electrolyte. The rather sharp drop in efficiency with concentration was not expected. Some decrease would be expected because of the increased IR drop in the solution and hence lower run-out voltages. However, the shapes of the curves were very similar to curve 1 of Figure 1 and the 2.0V end-point was again in the steep portion of the curve. The efficiency is related to the amount of  $\text{KClO}_4$  present, since decreasing the volume of electrolyte by one half had the same effect as decreasing the concentration by one half. Increasing the amount of electrolyte above 25 ml had little effect. The reason for these concentration effects is not known.

TABLE X

Effect of Varying  $\text{KClO}_4$  Molarity in DMSO

Mix Composition: 3:1  $\text{I}_2\text{O}_5:\text{C}$       Dry Mix 1.6g    1300 psi

Molarity	Minutes to 2.0 Volt	% Coulombic Efficiency
1	147	6.4
0.5	98	4.3
0.25	65	2.9
0.1	23	1.0

### OTHER CATHODE TREATMENTS

Cathodes were made with naphthalene incorporated in the mix, in the hope that solution of the naphthalene by DMSO would open up a larger surface area for reaction. This hope, however, was disappointed. Several variations of the technique were tried, but without success. Attempts were made to secure a more rapid and complete penetration of cathode by electrolyte through a vacuum impregnation process, but again no improvement in runout resulted.

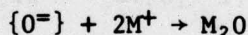
# ATTEMPTS TO DETERMINE THE FATE OF THE OXYGEN ON REDUCTION OF $I_2O_5$

It was assumed at the beginning, in the simplest fashion, that reduction of  $I_2O_5$  would occur by some such mechanism as:

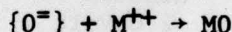


This is supported by the observation that  $I_2$  is formed as soon as current flows in the cell.

The species written as  $\{O^-\}$  is almost certainly not a simple oxide ion; however, some equivalent species, perhaps complexed with solvent, must appear in any reduction process. It was conjectured that a species such as  $\{O^-\}$  might form an insoluble metallic oxide by a reaction such as



or



Since both  $ZnO$  and  $Li_2O$  (prepared by dehydration of  $LiOH$ ) were found to be insoluble in DMSO, the oxides of these metals might be detected in the cathode by X-ray diffraction after extensive discharge of cells containing  $Li$  or  $Zn$  anodes and  $I_2O_5$ -carbon cathodes.

(a) The cell  $Li/DMSO, LiBr/I_2O_5-C$  was left on short circuit for several days; after this lapse of time, from the averaged current passed, one might expect appreciable amounts of  $Li_2O$ , if indeed it did form by the mechanism assumed above. The cathode was removed, washed with DMSO to remove  $LiBr$ , then with dry ether, and dried in vacuo. X-ray diffraction disclosed  $LiIO_3$  (~90%) as the major component, but with no evidence of  $Li_2O$ , or of  $LiOH$  which might arise from the oxide by reaction with moisture during handling.

(b) Discharge of the cell  $Li/DMSO, KClO_4/I_2O_5-C$  similarly gave  $KIO_3$  and  $LiIO_3$  as major and minor components of the cathode, but again no trace of  $Li_2O$  or  $K_2O$ , or of the corresponding hydroxides.

(c) The cell  $Zn/DMSO, KClO_4, 0.3M ZnCl_2/I_2O_5-C$  was discharged. In this cell the two lithium anodes were replaced by two sheets of zinc of the same size. On spontaneous discharge both current and voltage were very low and

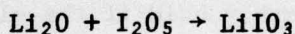


an excessive period of time would have been required before an appreciable cathodic reduction could occur. Attempts to drive the cell externally at 20-30 mA resulted in zinc deposition on the cathode. The ready oxidation of finely divided zinc on exposure to air would vitiate any attempt to demonstrate the presence of ZnO from a hypothetical reaction  $\text{Zn}^{++} + \{\text{O}^-\} \rightarrow \text{ZnO}$ . A very low forced discharge at 6 mA was conducted for several days, without zinc formation; however, examination of the cathode revealed  $\text{Zn}(\text{IO}_3)_2$  instead of the expected ZnO.

These experiments show that no metal oxides were formed; only iodates were detected. Also it is known from Figure 1 that  $\text{KIO}_3$  is electrochemically inactive and the same was demonstrated for  $\text{LiIO}_3$ . The question then arises how the iodates were formed.

The following series of experiments demonstrate that iodates produced in the above experiments could be formed non-electrochemically by the reaction of  $\text{I}_2\text{O}_5$  and cell constituents.

(1) 1.5g  $\text{I}_2\text{O}_5$  and .075g  $\text{Li}_2\text{O}$  were shaken together several days in 10 ml DMSO. This 20:1 weight ratio corresponded to a 1.8:1 molecular ratio for the reaction:



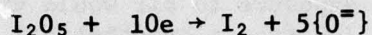
The white residue remaining at the end of shaking, after washing with DMSO and ether, was found to be a mixture of only  $\text{LiIO}_3$  and  $\text{I}_2\text{O}_5$ , suggesting that the reaction above had gone quantitatively, converting all the  $\text{Li}_2\text{O}$  to  $\text{LiIO}_3$  and leaving unreacted the excess of  $\text{I}_2\text{O}_5$  over the 1:1 molar ratio.

(2)  $\text{I}_2\text{O}_5$  shaken with 1M  $\text{KClO}_4$  or saturated  $\text{LiBr}$  in DMSO gave a white deposit approximately 95%  $\text{KIO}_3$  and 100%  $\text{LiIO}_3$  respectively, with no sign of  $\text{I}_2\text{O}_5$  remaining, while  $\text{I}_2\text{O}_5$  shaken with DMSO alone left a sticky residue of unreacted starting material.

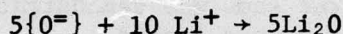
(3)  $\text{I}_2\text{O}_5$  (1g) and  $\text{ZnCl}_2$  (0.3g) reacted in DMSO to give a white precipitate of  $\text{Zn}(\text{IO}_3)_2$ .

There is then evidence that potassium, lithium, and zinc compounds, both soluble salts and insoluble oxides, react with  $\text{I}_2\text{O}_5$  in DMSO to form the corresponding iodates, which are not reducible electrochemically.  $\text{I}_2\text{O}_5$  and  $\text{Li}_2\text{O}$  might be expected to react, as these compounds are an acidic and a basic anhydride; the nature of the reaction of  $\text{I}_2\text{O}_5$  with a neutral salt such as  $\text{KClO}_4$  is not understood. In any case, the experiments above explain why the search for metallic oxides as reaction products of the hypothetical  $\{\text{O}^-\}$  was unsuccessful.

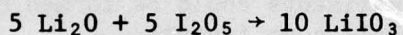
Considering the electrochemical reaction, further consequence of the work appeared; namely that even if an electrochemical reduction did proceed as written previously:



this could be followed by the rapid successive reactions:

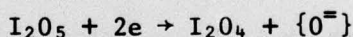


and



with the result that for each molecule of  $\text{I}_2\text{O}_5$  reduced electrochemically, five will be consumed in the subsequent acid-base neutralization to produce insoluble and unreactive  $\text{LiIO}_3$ , so that the greatest realizable coulombic efficiency is at one step reduced to 1/6 of the theoretical, or 17%. Similar considerations would presumably hold if the electrolyte contained  $\text{K}^+$  instead of  $\text{Li}^+$ .

These arguments would still hold even if the initial reaction did not proceed as far as  $\text{I}_2$ . Thus one might have a reaction formally expressible as:



(a great number of  $\text{I}_2\text{-O}_2$  compounds have been reported, including  $\text{I}_2\text{O}_4$ ). In this case the same sequence of reactions would follow, starting from  $\{\text{O}^-\}$ , again consuming  $\text{I}_2\text{O}_5$ , and with the same final result, that electrochemical utilization of  $\text{I}_2\text{O}_5$  would be well below theoretical.

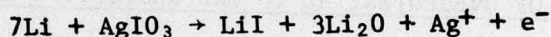
Apart from this,  $\text{K}^+$  and  $\text{Li}^+$ , as shown above, enter into direct non-electrochemical reaction with  $\text{I}_2\text{O}_5$  to form unreactive iodates which in addition to consuming  $\text{I}_2\text{O}_5$  can also block the surface, resulting in further diminution in utilization.

These various reactions can account for the very low efficiency of  $\text{I}_2\text{O}_5$  discharge, and appear to impose a fundamental limitation on the output of the  $\text{I}_2\text{O}_5$  cathode. This also suggests that the 12% utilization at low drain reported in Table IX is approaching three-quarters of the maximum utilization that could be expected in any circumstances.



Apart from these limitations resulting from successive reactions, it is evident that the initial electrochemical step is itself complex; also, a number of unusual phenomena - the extreme specificity as to solvent and electrolyte, effects of varying temperature and stand time, the great dependence of performance on concentration of  $\text{KClO}_4$  - must find an explanation in the solution of  $\text{I}_2\text{O}_5$  in DMSO and a subsequent presumably non-electrochemical reaction between solvent and solute.

Our finding that  $\text{KIO}_3$  is electrochemically inactive is at variance with more recent non-aqueous battery work, employing as depolarizer silver iodate,  $\text{AgIO}_3$  (16). The electrolyte was butyrolactone- $\text{LiAlCl}_4$ . The authors report good utilization (58%) based on a six-electron reduction,  $\text{IO}_3^- \rightarrow \text{I}^-$ . Both  $\text{LiI}$  and  $\text{Li}_2\text{O}$  were detected by X-ray analysis. The overall reaction is apparently representable as



(as a complex formed with the electrolyte, probably of the form  $\text{AgCl}_2^-$ ). The reason for this difference may lie in the capacity of the silver ion to complex and so be solubilized. The question could presumably be settled by discharge experiments with  $\text{AgIO}_3$  in the media used in this work, DMSO- $\text{KClO}_4$  or DMF- $\text{KClO}_4$ .

#### POLARIZATION EXPERIMENTS

These experiments had the object of separating out the factors that contribute to polarization, i.e. any effect that reduces the working voltage of a cell below the open circuit value, and so lessens the energy density.

#### CONCENTRATION OVERPOTENTIAL

Effects associated with concentration overpotential are the result of a concentration gradient developed in the cell during discharge, and should be reduced or eliminated by stirring the electrolyte. Stirring had in fact no effect on performance, suggesting, contrary to Knapp's results, that concentration overpotential does not play a significant role. Further work is needed to explain this discrepancy.

### RESISTIVE OVERPOTENTIAL

With the cell geometry and discharge conditions used in this work, this amounted to roughly 0.3 volts, as indicated by the instantaneous fall and rise in cell voltage on applying load and on reverting to open circuit conditions.

### ATTRIBUTION OF OVERPOTENTIAL TO THE RESPECTIVE ELECTRODES

These experiments were carried out with the three-electrode cell shown schematically in Figure 2. A is a common electrode, which in one arrangement is a lithium anode. The outer electrodes B and C are then  $I_2O_5$  cathodes. A current of 25 mA was passed between A and B (the "working" cathode) so that the cell A-B progressively discharged, while C, the "reference" cathode was kept on open circuit. The voltages of the couples A-B and A-C were followed during discharge. Periodically, current was passed for brief intervals through the couple A-C, A-B then reverting to open circuit. From the rises and falls in the voltage of the two couples information could be derived about the polarization of both cathode and anode at any time during the discharge. A corresponding experiment was carried out with another arrangement in which the common electrode A was now an  $I_2O_5$  cathode, B and C being "working" and "reference" lithium anodes.

Examples of the curves obtained are shown in Figure 3, with a common lithium anode, and Figure 4 with a common  $I_2O_5$  cathode. The upper curve in each figure shows the potential of the couple A-C (reference-common) and the lower curve the couple A-B (working-common). These are referred to as  $V(A-C)$  and  $V(A-B)$  respectively. The spikes show the voltage displacements during the brief switching periods, when B and C electrodes reverse their roles. The initial open circuit voltage for the couples A-B and A-C are, of course, identical. These are indicated by the large filled circles on the ordinate axis.

The lower curves  $V(A-B)$  in Figure 3 and 4 represent cell voltage during discharge; they follow the same general course and would coincide if the cells were identical. They both exhibit an immediate initial drop of 0.4 volts from open circuit on first applying current and a steady decline thereafter.

Examining first Figure 3 (common lithium anode) one observes that on establishing the current across A-B,  $V(A-C)$  falls about 0.1 volts at once and then remains unchanged throughout discharge. This is evidently ascribable entirely to the common lithium anode and is probably an activation overpotential. Hence the progressive fall in  $V(A-B)$  as discharge proceeds must



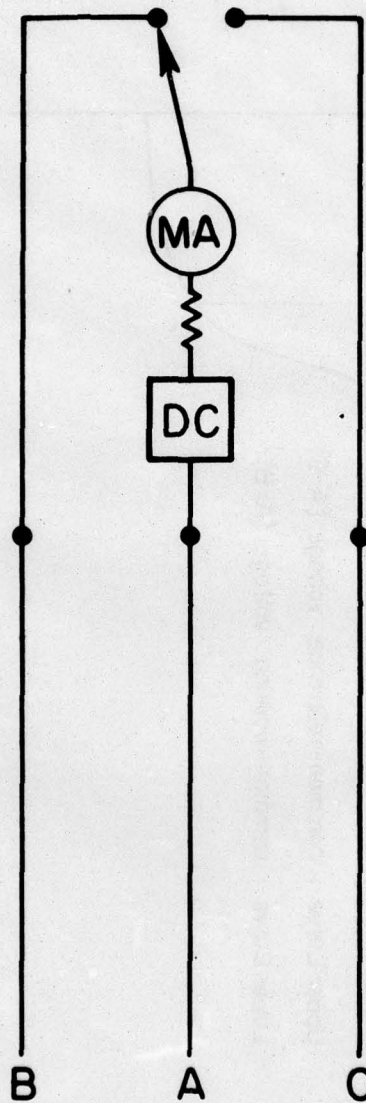


Fig. 2: Schematic representation of apparatus used for polarization experiments. Current normally passes through electrode B.

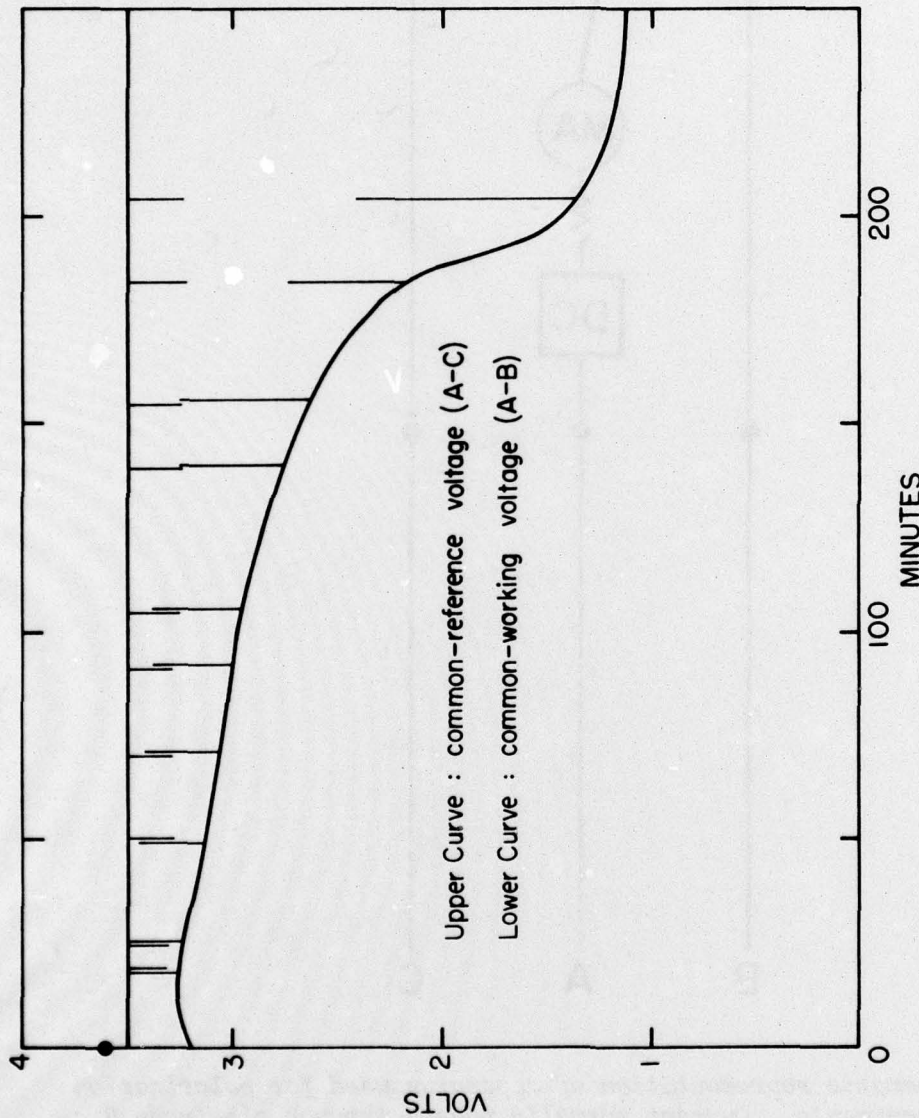


Fig. 3: Polarization experiments, one lithium anode (A) located between a working (B) and a reference (C)  $I_{2O_5}$  cathode. A and B are discharged at 25 mA, C is left on open circuit. Voltages A-B and A-C are recorded continuously. Spikes indicate voltage shifts when C is discharged for brief intervals in place of B. One spike of each pair has for clarity been displaced slightly along the time axis. Solid point on ordinate ( $t = 0$ ) indicates initial open circuit voltage.



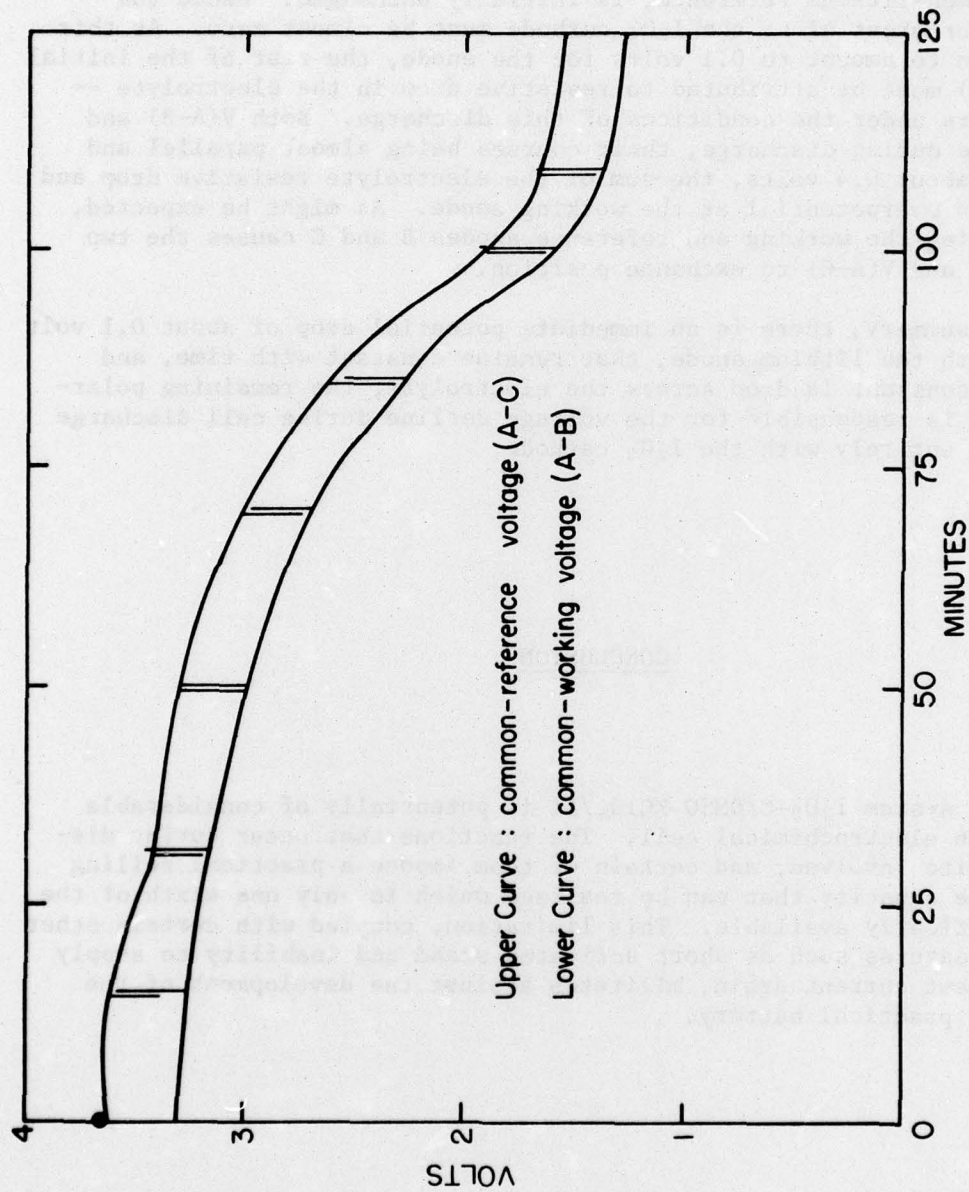


Fig. 4: Polarization experiments, as in Figure 3, with one  $I_2O_5$  cathode (A) located between a working (B) and a reference (C) lithium anode. Discharge conditions and significance of voltage shifts are as described for Figure 3.

be due to the  $I_2O_5$  cathode. This is supported by the successively larger recoveries in  $V(A-B)$  during discharge when the working  $I_2O_5$  cathode is exchanged for the (nearly undischarged) reference  $I_2O_5$  cathode.

Figure 4 reinforces these conclusions. On applying current,  $V(A-C)$ , i.e.  $I_2O_5$  common-lithium reference, is initially unchanged. Hence the activation overpotential at the  $I_2O_5$  cathode must be almost zero. As this has been shown to amount to 0.1 volts for the anode, the rest of the initial drop in  $V(A-B)$  must be attributed to resistive drop in the electrolyte -- about 0.3 volts under the conditions of this discharge. Both  $V(A-B)$  and  $V(A-C)$  decline during discharge, their courses being almost parallel and separated by about 0.4 volts, the sum of the electrolyte resistive drop and the activation overpotential at the working anode. As might be expected, then, exchanging the working and reference anodes B and C causes the two curves  $V(A-B)$  and  $V(A-C)$  to exchange position.

In summary, there is an immediate potential drop of about 0.1 volt associated with the lithium anode, that remains constant with time, and another also constant IR drop across the electrolyte; the remaining polarization which is responsible for the voltage decline during cell discharge is associated entirely with the  $I_2O_5$  cathode.

#### CONCLUSION

The system  $I_2O_5-C/DMSO-KClO_4/Li$  is potentially of considerable interest as an electrochemical cell. The reactions that occur during discharge are quite involved, and certain of them impose a practical ceiling on the cathode capacity that can be realized which is only one sixth of the amount theoretically available. This limitation, coupled with certain other undesirable features such as short activated stand and inability to supply more than modest current drain, militates against the development of the system into a practical battery.

#### ACKNOWLEDGEMENTS

The authors are grateful to Mr. P. Miasek and Ms. C. Anderson for skilled technical assistance.



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1. ORIGINATING ACTIVITY <b>Defence Research Establishment Ottawa</b> <b>National Defence Headquarters</b> <b>Ottawa, Ontario, Canada K1A 0Z4</b>		2a. DOCUMENT SECURITY CLASSIFICATION <b>UNCLASSIFIED</b>
		2b. GROUP <b>N/A</b>
3. DOCUMENT TITLE  <b>LITHIUM BATTERY SYSTEMS: EXAMINATION OF THE IODINE PENTOXIDE CATHODE (U)</b>		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) <b>REPORT</b>		
5. AUTHOR(S) (Last name, first name, middle initial)  <b>COLEMAN, John R. and NAGY, Gerard D.</b>		
6. DOCUMENT DATE <b>MAY 1977</b>	7a. TOTAL NO. OF PAGES <b>23</b>	7b. NO. OF REFS <b>16</b>
8a. PROJECT OR GRANT NO.  <b>54-80-08</b>	9a. ORIGINATOR'S DOCUMENT NUMBER(S)  <b>DREO REPORT NO. 760</b> ✓	
8b. CONTRACT NO.	9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)	
10. DISTRIBUTION STATEMENT  <b>UNLIMITED DISTRIBUTION</b>		
11. SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY	
13. ABSTRACT <p>The electrochemical system lithium-iodine pentoxide, attractive because of its high theoretical energy density, was investigated, employing as electrolyte a variety of salts dissolved in polar organic solvents. Iodine pentoxide blended with graphite and pressed on an expanded silver grid served as cathode; the anodes were made by pressing lithium ribbon onto an expanded nickel grid.</p> <p>Of the salt-solvent combinations tried, potassium perchlorate dissolved in dimethylsulfoxide was most satisfactory; even with this combination the fraction of the theoretical energy density realized amounted at most to about 12%. Chemical investigations showed that iodine pentoxide in dimethylsulfoxide may enter into several kinds of reactions, all of which lead to its conversion to the electrochemically inactive iodate ion. One sixth or 17% of the pentoxide appeared to be the most that can in fact be discharged. This fact, coupled with its poor activated stand properties and moderate drain capability make it improbable that the system could be developed into a practical battery.</p> <p style="text-align: center;">UNCLASSIFIED</p>		



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